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XXVII. *Researches on a New Class of Alcohols.*

By AUGUSTUS WILLIAM HOFMANN, LL.D., F.R.S., and AUGUSTUS CAHOUS, F.C.S.

Received May 15,—Read June 18, 1857.

ON submitting glycerin to destructive distillation, either alone or in the presence of bisulphate of potassium or anhydrous phosphoric acid, a very remarkable product is obtained, which has been elaborately studied by Professor REDTENBACHER.

According to the researches of this distinguished chemist, this substance, to which the name of acrolein has been given, presents all the characters of an aldehyde, and bears, in its reactions, a close resemblance to the vinic aldehyde. Under the influence of oxidizing agents, and especially of oxide of silver, this body changes into an acid which REDTENBACHER designates by the name "Acrylic Acid," and which stands to acrolein in the same relation that acetic acid bears to common aldehyde.

The researches of MM. WILL and WERTHEIM upon the volatile oils of garlic and mustard established a relationship between these compounds and acrolein which has been rendered still more evident by the recent investigations of MM. BERTHELOT and DE LUCA.

In studying the action of iodide of phosphorus upon glycerin, these chemists obtained a volatile liquid containing iodine, the composition of which is expressed by the formula  $C_6H_5I$ , and to which they applied the name Iodide of propylene.

This substance is evidently allied to the chloride of propylene,  $C_6H_5Cl$ , and bromide of propylene,  $C_6H_5Br$ , discovered previously by CAHOUS, REYNOLDS and HOFMANN, in studying the action of chlorine and bromine on the gases which are obtained by submitting either amylic alcohol or valeric acid, as well as their higher homologues, to the action of heat.

A glance at the formulæ of the propylene-compounds, and the volatile oils of garlic and mustard, viz.

Chloride of propylene . . .	$C_6H_5Cl$ ,
Bromide of propylene . . .	$C_6H_5Br$ ,
Iodide of propylene . . .	$C_6H_5I$ ,
Garlic oil . . . . .	$C_6H_5S$ ,
Mustard oil . . . . .	$C_6H_5C_2NS_2$ ,

obviously shows that the same radical Allyl,  $C_6H_5$ , may be assumed to exist in all these compounds.

This relation did not escape REYNOLDS, who, in his memoir published about six years

ago\*, distinctly sets forth the probability of the transformation of the chloride and bromide of propylene into the oils of garlic and mustard by the action respectively of the sulphide and sulphocyanide of potassium.

The experimental proof of the correctness of this idea was however reserved for MM. BERTHELOT and DE LUCA, and for M. ZININ. In fact these chemists demonstrated that the action of iodide of propylene upon the sulphocyanide of potassium or silver, gives rise to an oil which is absolutely identical with that furnished by distilling the seeds of the common mustard (*Sinapis nigra*) with water.

The admission of a radical allyl ( $C_6H_5$ ) analogous to ethyl ( $C_4H_5$ ), establishes a perfect analogy between the compounds derived from propylene and glycerin, and the several terms of the ethyl-series.

Ethyl-series.		Allyl-series.	
$C_4H_5Cl$	Chloride	$C_6H_5Cl$	
$C_4H_5Br$	Bromide	$C_6H_5Br$	
$C_4H_5I$	Iodide	$C_6H_5I$	
$C_4H_5S$	Sulphide	$C_6H_5S$	
$C_4H_5, C_2NS_2$	Sulphocyanide	$C_6H_5C_2NS_2$	
$C_4H_6O_2$	Alcohol		
$C_4H_4O_2$	Aldehyde	$C_6H_4O_2$	
$C_4H_4O_4$	Acid	$C_6H_4O_4$	

There yet remained the key-stone to be inserted into this edifice, in other words, the alcohol had still to be discovered, to which not only all the preceding compounds could be referred, but which might serve in producing a long series of substances analogous to the host of compound ethers derived from common alcohol.

After many attempts, which remained long unsuccessful on account of the facility with which this class of bodies is altered, we at last succeeded in obtaining, not only the alcohol and ether of this series (for which we have adopted the name of the "Allyl-series†"), but also a very considerable number of compound ethers, and some of their derivatives.

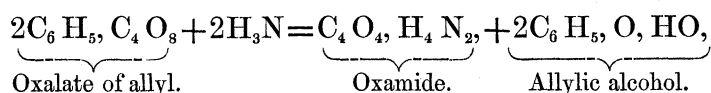
In order to arrive at this result, we have submitted many silver-salts to the action of iodide of allyl, expecting to obtain by double decomposition iodide of silver and a compound ether, from which it would be possible afterwards to extract the alcohol. The silver-salts are in general powerfully attacked by iodide of allyl, but comparatively

\* Quarterly Journal of the Chemical Society, vol. iii. p. 111, 1851.

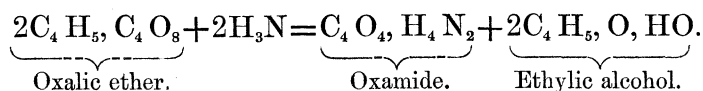
† In a preliminary note communicated some time ago to the Royal Society (Proceedings, vol. viii. No. 19), regarding the principal facts detailed in the present memoir, we adopted the term "Acryl-series;" but as the name acryl belongs more properly to the derived radical which may be assumed to exist in acrolein, we now prefer the appellation "Allyl-series," in accordance with the nomenclature originally adopted by MM. WILL and WERTHEIM. This name has also been adopted in several papers which appeared after the above-mentioned notice had been published.

few of the products obtained in this reaction are themselves appropriate for the separation of allylic alcohol. The most satisfactory results we have obtained with oxalate of allyl. Iodide of allyl acts very energetically upon oxalate of silver. After several hours' digestion at  $100^{\circ}$ , which is most conveniently accomplished in the presence of anhydrous ether, the reaction is completed. The oxalate of allyl furnished by this process can be easily purified; on filtering the ethereal liquor from the iodide of silver and distilling, the ether passes over first, the temperature then rises rapidly, and between  $206^{\circ}$  and  $207^{\circ}$ , a colourless transparent liquid distils over, which is the oxalate of allyl. According to an analysis, the details of which will be given further on, this ether contains  $C_{16}H_{10}O_8 = 2C_6H_5, C_4O_8$ .

When once the oxalate of allyl has been procured, nothing is easier than to separate from it the allylic alcohol. It is only necessary to treat this product with an excess of dry ammonia, by which oxamide and the allylic alcohol are obtained, according to the following equation:—



a result in perfect accordance with the reciprocal action of ammonia and oxalic ether.



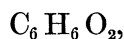
The alcohol separated by distillation from the oxamide is not absolutely pure—it may retain water and ammonia; but a simple rectification over anhydrous sulphate of copper is sufficient to render it perfectly pure.

Allylic alcohol is a colourless, very mobile liquid, possessing a pungent odour, recalling at the same time that of common alcohol and of mustard oil. It boils at  $103^{\circ}C$ ., and is combustible, but burns with a far more luminous flame than ordinary alcohol. Its flavour is spirituous and pungent. Water, alcohol and wood-spirit dissolve it in all proportions.

The analysis of allylic alcohol has furnished the following results:

0.182 grm. of substance gave 0.414 grm. of carbonic acid and 0.172 grm. of water.

The percentage composition corresponding to these numbers leads to the formula

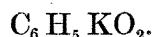


which requires—

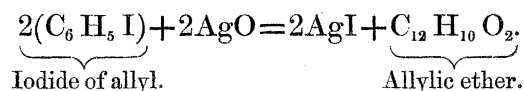
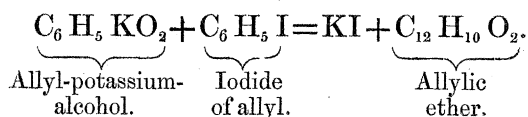
	Theory.		Experiment.
6 equivs. of Carbon . .	36	62.07	62.08
6 equivs. of Hydrogen .	6	10.34	10.43
2 equivs. of Oxygen . .	16	27.59	—
1 equiv. of Allylic alcohol	58	100.00	

Accordingly, allylic alcohol has the same composition as acetone and propylic aldehyde, from both of which substances it nevertheless essentially differs.

Potassium and sodium attack allylic alcohol energetically, especially if the temperature be slightly raised; hydrogen is copiously evolved, and a gelatinous substance is formed obviously analogous to potassium-alcohol, the composition of which must accordingly be represented by the formula



On treating this last product with iodide of allyl, much heat is evolved, iodide of potassium is deposited in abundance, and at the same time there is formed a colourless volatile liquid, very mobile, lighter than water, and entirely insoluble in that menstruum, which corresponds both in composition and reactions to ordinary ether. This compound, which we will designate by the term allylic ether, and which boils at  $82^\circ\text{C}.$ , also results from the reaction of iodide of allyl on the oxides of silver and mercury. The following equations represent these reactions:—

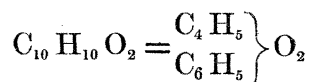


On treating ethylic potassium-alcohol with iodide of allyl, or allylic potassium-alcohol with iodide of ethyl, iodide of potassium is deposited, a colourless, aromatic, very volatile liquid being formed, which boils at about  $64^\circ\text{C}.$ , and is a mixed ether containing both the radicals ethyl and allyl.

The analysis of this substance has furnished the following results:—

0.338 grm. of substance gave 0.864 grm. of carbonic acid and 0.352 grm. of water.

The formula



requires the following values:—

	Theory.		Experiment.
10 equivs. of Carbon . . .	60	69.76	69.69
10 equivs. of Hydrogen . . .	10	11.62	11.56
2 equivs. of Oxygen . . .	16	18.62	—
	<u>86</u>	<u>100.00</u>	

Methyl-, amyl- and phenyl-potassium-alcohols, when brought in contact with iodide of allyl, furnish analogous results.

By distilling allylic alcohol with the chloride, bromide or iodide of phosphorus, the hydrochloric, hydrobromic and hydriodic ethers of this series are obtained with the

utmost facility. Iodide of allyl obtained by this process, possesses all the properties of the iodide of propylene which is produced by the action of iodide of phosphorus on glycerin; and in a similar manner the chloride and bromide of allyl, and the chloride and bromide of propylene, are identical in every respect.

Allylic alcohol dissolves without colour in concentrated sulphuric acid, and gives rise to a conjugate acid, which forms soluble and crystalline salts with baryta, strontia, and oxide of lead.

Anhydrous phosphoric acid powerfully attacks allylic alcohol at a moderate temperature, a colourless gas being disengaged which burns with a very luminous flame. Its analysis has not been made, but most probably it is a hydrocarbon represented by the formula  $C_6H_4$ .

Allylic alcohol is readily acted upon by oxidizing agents. A mixture of bichromate of potassium and sulphuric acid attacks this body with extreme violence. The products of the reaction are acrolein and allylic acid. The same transformation is effected by platinum-black, though more slowly. Lastly, this alcohol, when treated with potassa and bisulphide of carbon, gives rise to a compound which crystallizes in beautiful yellow needles, resembling xanthate of potassium, and to which analysis will probably assign an analogous formula.

#### *Sulphide of Allyl (Essence of Garlic).*

When iodide of allyl is allowed to fall drop by drop into a concentrated alcoholic solution of protosulphide of potassium, a very energetic action ensues, the liquid becomes very hot, and an abundant crystalline deposit takes place of iodide of potassium. It is important that the iodide of allyl should only be added gradually, to avoid spirting, by which a part of the product would be lost. As soon as the action ceases, the liquid is mixed with a slight excess of sulphide of potassium; on the addition of water a light yellowish limpid oil separates, possessing a strong smell of garlic. When rectified, this liquid becomes colourless; it boils at  $140^{\circ}C.$ , and gives with nitrate of silver a crystalline precipitate soluble in a boiling mixture of alcohol and water, and separating from this solvent in the form of beautiful white needles, absolutely identical with those which the natural essence of garlic produces. Sulphide of allyl also comports itself with corrosive sublimate and bichloride of platinum, exactly like the natural garlic oil.

On analysis sulphide of allyl gave the following results:—

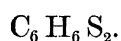
0.420 grm. of substance yielded 0.975 grm. of carbonic acid and 0.338 grm. of water.

The formula  $C_{12}H_{10}S_2 = 2C_6H_5S$ , requires the following values:—

	Theory.		Experiment.
12 equivs. of Carbon . . . .	72	63.16	63.3
10 equivs. of Hydrogen . . . .	10	8.78	8.9
2 equivs. of Sulphur . . . .	32	28.06	—
1 equiv. of Sulphide of allyl . .	114	100.00	

*Allylic Mercaptan.*

When in the process for the preparation of the preceding compound the protosulphide of potassium is replaced by the hydrosulphate of sulphide of potassium, a volatile product is obtained, having a similar but more ethereal odour. This substance acts with energy upon oxide of mercury, with which it forms a compound dissolving in boiling alcohol and separating from it on cooling in the form of pearly scales of remarkable brilliancy, which present the greatest resemblance to mercaptide of mercury. The liquid obtained in the above-mentioned reaction boils at  $90^{\circ}\text{C}.$ , and possesses a composition and an aggregate of properties which closely resemble those of the mercaptan of the ethyl-series, being in fact the allylic mercaptan,



Submitted to analysis, this compound furnished the following results:—

I. 0.500 grm. of substance gave 0.896 grm. of carbonic acid and 0.371 grm. of water.

II. 0.300 grm. gave 0.536 grm. of carbonic acid and 0.226 grm. of water.

		Theory.		Experiment.	
				I.	II.
6 equivs. of Carbon	36	48.65		48.86	48.71
6 equivs. of Hydrogen	6	8.11		8.23	8.30
2 equivs. of Sulphur	32	43.24		—	—
1 equiv. of Allylic mercaptan	74	100.00			

This compound is powerfully attacked by nitric acid with disengagement of binoxide of nitrogen; the liquid assumes a red colour in the same manner as ethylic mercaptan, the product of the reaction being a peculiar acid, analogous to ethyl-sulphurous acid, which forms with baryta a salt crystallizing in brilliant white scales.

*Sulphallylic Acid.*

When allylic alcohol is added in small quantities at a time to about its own volume of monohydrated sulphuric acid, the mixture becomes heated without being sensibly coloured. If the acid liquor be diluted with about seven to eight times its volume of water, and then neutralized with carbonate of barium in fine powder, there is obtained on evaporation a substance which crystallizes in brilliant white laminae.

This salt, which is formed under the very same conditions as sulphovinate of barium, furnished on analysis the following results:—

0.154 grm. of substance yielded 0.087 grm. of sulphate of barium, which represents 33.11 per cent. of barium.

The formula



requires—

	Theory.		Experiment.
6 equivs. of Carbon . . . . .	36	17·54	—
5 equivs. of Hydrogen . . . . .	5	2·43	—
1 equiv. of Barium . . . . .	68·5	33·33	33·11
2 equivs. of Sulphur . . . . .	32	15·65	—
8 equivs. of Oxygen . . . . .	64	31·15	—
1 equiv. of Sulphallylate of barium	205·5	100·00	

*Oxalate of Allyl and Allyloxamethan.*

We have previously stated under what circumstances oxalate of allyl is formed, we will not therefore recur again to its mode of preparation. Purified by a simple rectification, this compound presents itself as a colourless limpid liquid of a specific gravity of 1·05 at 15°·5 C., and boiling constantly between 206° and 207° C. (Bar. 0<sup>m</sup>·754), possessing an aromatic odour recalling that of oxalic ether, with a faint admixture of the smell of mustard oil. A similar remark in fact applies to all the allyl-compounds; they smell like the corresponding ethyl-compounds, only somewhat more pungent. When mixed with water, oxalate of allyl undergoes gradual decomposition, but it is much more rapidly decomposed when boiled with a solution of caustic potassa. Solution of ammonia attacks it rapidly, and transforms it into oxamide and allylic alcohol. An alcoholic solution of ammonia added with caution so as to avoid the formation of oxamide, produces a substance analogous to oxamethan, which, for this reason, we shall designate by the name allyloxamethan. This substance separates in magnificent crystals when its alcoholic solution is allowed to evaporate spontaneously.

Potassium and sodium energetically attack the oxalate of allyl, especially with the aid of heat, an evolution of carbonic oxide ensues, whilst there passes over on distillation a limpid colourless oil of an aromatic odour, lighter than water; this is in fact the carbonate of allyl.

The analysis of the oxalate of allyl has furnished the following results:—

I. 0·179 grm. of substance gave 0·3695 grm. of carbonic acid and 0·0951 grm. of water.

II. 0·320 grm. of a second specimen gave 0·662 grm. of carbonic acid and 0·170 grm. of water.

The formula  $C_{16} H_{10} O_8 = 2C_6 H_5, C_4 O_8$

requires the following values:—

	Theory.		Experiment.	
			I.	II.
16 equivs. of Carbon . . . . .	96	56·47	56·31	56·40
10 equivs. of Hydrogen . . . . .	10	5·88	5·92	5·89
8 equivs. of Oxygen . . . . .	64	37·65	—	—
1 equiv. of Oxalate of allyl	170	100·00		



The analysis of a perfectly crystallized specimen of allyloxamethan gave the subjoined numbers.

0.532 grm. of substance gave 0.903 grm. of carbonic acid and 0.266 grm. of water.

The formula



requires the following numbers, which we place in juxtaposition with the experimental percentages:—

	Theory.		Experiment.
10 equivs. of Carbon . . .	60	46.51	46.29
7 equivs. of Hydrogen . . .	7	5.42	5.55
1 equiv. of Nitrogen . . .	14	10.84	—
6 equivs. of Oxygen . . .	48	37.23	—
1 equiv. of Allyloxamethan .	129	100.00	

#### *Acetate of Allyl.*

Iodide of allyl, when brought in contact with acetate of silver, becomes strongly heated, producing iodide of the metal and a liquid of an aromatic odour which closely resembles that of acetic ether. The crude product obtained in this way is not pure; it always retains a certain quantity of the iodide of allyl, from which it is purified by one or two rectifications over a fresh quantity of acetate of silver.

Thus prepared, acetate of allyl is a colourless liquid, lighter than water, possessing a pungent aromatic smell, and boiling between 98° and 100° C. Potassa decomposes it at the boiling temperature, giving rise to the formation of acetate of potassium and reproducing allylic alcohol.

Submitted to analysis this substance furnished the following results:—

I. 0.500 grm. of acetate of allyl gave 1.100 grm. of carbonic acid and 0.370 grm. of water.

II. 0.450 grm. of acetate of allyl gave 0.988 grm. of carbonic acid and 0.328 grm. of water.

These numbers represent the formula



	Theory.	Experiment.	
		I.	II.
10 equivs. of Carbon . . .	60	60.00	59.87
8 equivs. of Hydrogen . . .	8	8.24	8.09
4 equivs. of Oxygen . . .	32	—	—
1 equiv. of Acetate of allyl .	100		

#### *Butyrate of Allyl.*

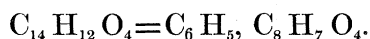
Iodide of allyl becomes strongly heated when brought in contact with butyrate of silver; when the mixture is distilled, an amber-coloured liquid is collected which becomes colourless by rectification. This liquid is oily, very limpid, lighter than water, boils at about 140° C., and has an odour like that of butyric ether. Concentrated

solution of potassa, when assisted by heat, decomposes this ether rapidly, producing allylic alcohol and an alkaline butyrate.

On analysis this compound afforded the following results:—

- I. 0·400 grm. of substance gave 0·966 grm. of carbonic acid and 0·345 grm. of water.  
 II. 0·450 grm. of substance yielded 1·081 grm. of carbonic acid and 0·384 grm. of water.

These numbers may be translated into the formula



	Theory.		Experiment.	
			I.	II.
14 equivs. of Carbon . . .	84	65·62	65·86	65·51
12 equivs. of Hydrogen . . .	12	9·38	9·58	9·48
4 equivs. of Oxygen . . .	32	25·00	—	—
1 equiv. of Butyrate of allyl	128	100·00		

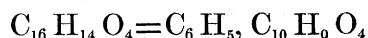
#### *Valerate of Allyl.*

Valerate of silver comports itself with iodide of allyl exactly like the acetate and butyrate: powerful reaction, attended by separation of iodide of silver, and production of an ethereal liquid which may be obtained pure by repeated rectification over fresh quantities of valerate of silver, washing with slightly alkaline water, and digestion over chloride of calcium.

Thus prepared, valerate of allyl is a colourless liquid which boils at 162°, and the aromatic odour of which recalls that of valerate of ethyl. It is lighter than water, insoluble in this menstruum, but readily dissolved by alcohol and ether. The vapour burns with a luminous flame.

0·384 grm. of substance gave 0·949 grm. of carbonic acid and 0·350 grm. of water.

The formula



requires—

	Theory.		Experiment.
16 equivs. of Carbon . . .	96	67·60	67·40
14 equivs. of Hydrogen . . .	14	9·86	10·12
4 equivs. of Oxygen . . .	32	22·54	—
1 equiv. of Valerate of allyl .	142	100·00	

#### *Benzoate of Allyl.*

Benzoate of allyl may be obtained either by the action of chloride of benzoyl on allylic alcohol, or by the action of iodide of allyl on benzoate of silver.

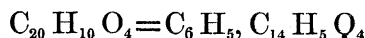
It is a nearly colourless liquid with a tinge of amber, heavier than water, in which fluid it is insoluble; it possesses an aromatic odour similar to that of benzoic ether, and boils at 228 C°. Alcohol, wood-spirit, and ether dissolve it freely.

A boiling aqueous solution of potassa decomposes it, reproducing allylic alcohol and benzoic acid which unites with the alkali.

The benzoate of allyl furnished on analysis the following results:—

0·372 grm. of substance gave 0·997 grm. of carbonic acid and 0·209 grm. of water.

The formula



requires—

	Theory.		Experiment.
20 equivs. of Carbon . . . .	120	74·07	73·10
10 equivs. of Hydrogen . . . .	10	6·17	6·24
4 equivs. of Oxygen . . . .	32	19·76	—
1 equiv. of Benzoate of allyl .	162	100·00	

### *Cyanate of Allyl.*

Cyanate of silver is rapidly attacked even in the cold by iodide of allyl, the heat generated by the reaction being sufficient to carry over nearly the whole of the product.

By this means a colourless very limpid liquid is obtained, boiling at 82°, possessing an extremely pungent odour, which, like that of cyanic ether, produces lacrymation in a high degree. When mixed with ammonia, this substance rapidly disappears, a gentle evolution of heat being perceptible, and the solution furnishes on evaporation a magnificently crystallized body which is the allylic urea. Ethylamine behaves in a similar manner with cyanate of allyl, and on evaporation beautiful prisms of ethyl-allyl-urea are obtained.

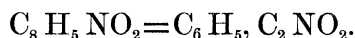
When submitted to analysis cyanate of allyl furnished the following results:—

I. 0·438 grm. of substance yielded 0·927 grm. of carbonic acid and 0·244 grm. of water.

II. 0·335 grm. of substance gave 0·926 grm. of carbonic acid and 0·184 grm. of water.

III. 0·381 grm. of substance gave 53 cub. cent. of nitrogen at the temperature of 10° C. and a pressure of 0<sup>m</sup>·761.

These results may be represented by the formula



	Theory.		Experiment.		
			I.	II.	III.
8 equivs. of Carbon . . . .	48	57·83	57·72	57·78	—
5 equivs. of Hydrogen . . . .	5	6·02	6·18	6·09	—
1 equiv. of Nitrogen . . . .	14	16·86	—	—	16·71
2 equivs. of Oxygen . . . .	16	19·29	—	—	—
1 equiv. of Cyanate of allyl .	83	100·00			

We have controlled the preceding formula by a determination of the density of the vapour of cyanate of allyl. The following are the details of observation:—

Temperature of the air . . . . . 12° C.

Temperature of vapour . . . . . 152° C.

Excess of weight of balloon filled with vapour, over

that of balloon filled with air . . . . . 0·386 grm.

Capacity of balloon . . . . .	292 cubic cent.
Barometer . . . . .	0 <sup>m</sup> ·762.
Remaining air . . . . .	0
∴ Weight of litre of vapour . . . . .	3·961 grms.
Experimental density of vapour . . . . .	3·045

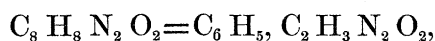
The weight represented by the formula  $C_8H_5NO_2$ , divided by the experimental density, furnishes the quotient  $\frac{83}{3\cdot045} = 27\cdot25$ .

For a condensation to four volumes of vapour, the more accurate number 28·92 should have been found. Thus it is obvious that the condensation to four volumes observed for most organic substances, obtains also with cyanate of allyl.

The theoretical density of the vapour of cyanate of allyl is  $\frac{83}{28\cdot92} = 2\cdot87$ .

### *Allyl-urea.*

The formation of this substance has already been mentioned. On submitting a solution of cyanate of allyl in ammonia to evaporation, a beautifully crystallized colourless substance is obtained which is soluble in water and alcohol. It contains



and differs therefore from thiosinamine only in having the sulphur of this substance replaced by an equivalent proportion of oxygen.

This compound, which presents the properties of a true urea, and is prepared under conditions which determine the production of this class of compounds, furnished the following results on analysis:—

I. 0·320 grm. of substance gave 0·561 grm. of carbonic acid and 0·234 grm. of water.

II. 0·275 of substance gave 66 cub. cent. of nitrogen at the temperature of 17° and under a pressure of 0<sup>m</sup>·759.

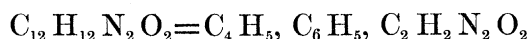
	Theory.	Experiment.	
		I.	II.
8 equivs. of Carbon . . . .	48	47·81	—
8 equivs. of Hydrogen . . .	8	8·11	—
2 equivs. of Nitrogen . . .	28	—	27·86
2 equivs. of Oxygen . . . .	16	—	—
1 equiv. of Allyl-urea . . .	100		

### *Ethyl-allyl-urea.*

On treating cyanate of allyl by solution of ethylamine, instead of ammonia, a series of perfectly analogous phenomena is observed. On cooling the fluid solidifies into a crystalline mass which dissolves in alcohol, and separates from this solution, on evaporation, in the form of beautiful prisms similar to those of allyl-urea. This substance, which constitutes the ethyl-allyl-urea, yielded on analysis the following results:—

0.500 grm. of substance gave 1.029 grm. of carbonic acid and 0.417 grm. of water.

The formula



requires—

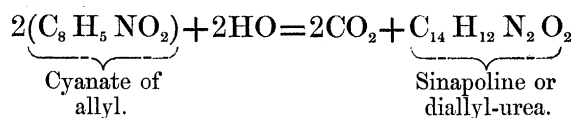
	Theory.		Experiment.
12 equivs. of Carbon . . .	72	56.25	56.12
12 equivs. of Hydrogen . . .	12	9.37	9.25
2 equivs. of Nitrogen . . .	28	21.95	—
2 equivs. of Oxygen . . .	16	12.43	—
1 equiv. of Ethyl-allyl-urea .	128	100.00	

The action of methylamine, of amylamine, and of aniline upon cyanate of allyl, has given us analogous results. We have not submitted these products to analysis; but their resemblance to the preceding compounds, and especially their mode of formation, leave no doubt respecting their composition. These products, as is obvious, belong to that numerous class of compound ureas which have been studied with such remarkable results by M. WURTZ.

#### *Diallyl-urea (Sinapoline).*

When cyanate of allyl is heated with water, it assumes a buttery consistence and ultimately solidifies entirely. The product obtained under these circumstances possesses all the properties of sinapoline, which, as is known, is formed by the action of hydrated protoxide of lead upon mustard oil, and is in fact diallyl-urea. The properties of this substance presenting complete identity with those of sinapoline, and its mode of formation being perfectly similar to that of dimethyl- and diethyl-urea, we have not thought it necessary to submit it to analysis. This body is likewise formed when cyanate of allyl is boiled with an aqueous solution of potassa, with the view of transforming it, after the manner of ordinary cyanic ether, into an alkaline carbonate and an ammonia-base. In this case it is necessary to arrest the action at a certain point, for if the ebullition be continued, the sinapoline is destroyed in its turn, producing carbonate of potassium and ammonia-bases.

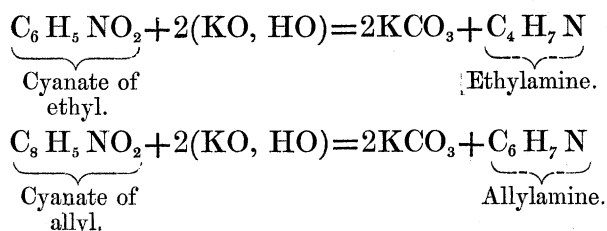
The formation of sinapoline, by the reciprocal action of cyanate of allyl and water, is represented by the following equation:—



#### *Allyl-ammonias.*

When cyanate of allyl is boiled with a concentrated solution of caustic potassa until the oily layer entirely disappears, a complete decomposition ensues, and the residue contains only a mixture of carbonate of potassium with an excess of the alkaline hydrate; the volatile products condensed in hydrochloric acid furnish a saline mass which may be

obtained crystallized by evaporation. This substance is always a mixture, of which the quality and quantity of the constituents are variable. The action of potassa on it always produces a base which is readily soluble in water, but also basic oils insoluble in water, the boiling-point of which rises as high as 180° C. Simple distillation of the liberated bases appears to give rise to decomposition, and thus to induce further complication. We have not succeeded in ascertaining with perfect precision the nature of this mixture, but we have found that it invariably contains a considerable quantity of a base which bears the same relation to allylic alcohol that is observed between ethylamine and ordinary alcohol. The formation of this substance, which we propose to designate *allylamine*, is perfectly analogous to the production of ethylamine by means of cyanate of ethyl,



But, as we have already said, the decomposition of the cyanate of allyl is far from presenting the same definite character as that of the corresponding compound of the ethyl-series.

Since it was impossible to separate the mixture of bases by a fractional distillation, we have determined the composition of allylamine by the analysis of the platinum-salt.

#### *Allylamine.*

On adding a solution of bichloride of platinum to the hydrochloric solution of the bases resulting from the action of potassa upon cyanate of allyl, there is produced almost invariably a pale yellow precipitate; and the solution filtered off from this precipitate deposits on evaporation a magnificent salt, crystallizing in brilliant orange-coloured needles. The pale precipitate\* varies in quantity and composition; but the second salt

\* This precipitate appears to be a mixture in variable proportions of the platinum-salts of ammonia and methylamine. The following are some determinations of the platinum in this precipitate:—

- I. 0·3405 grm. of the platinum-salt gave 0·1483 grm. of platinum.
- II. 0·26375 grm. of the platinum-salt gave 0·1150 grm. of platinum.
- III. 0·2945 grm. of the platinum-salt gave 0·1250 grm. of platinum.
- IV. 0·321 grm. of the platinum-salt gave 0·1357 grm. of platinum.
- V. 0·3345 grm. of the platinum-salt gave 0·1412 grm. of platinum.
- VI. 0·2205 grm. of the platinum-salt gave 0·0927 grm. of platinum.
- VII. 0·297 grm. of the platinum-salt gave 0·124 grm. of platinum.

#### Percentages.

I.	II.	III.	IV.	V.	VI.	VII.
43·61	43·6	42·44	42·27	42·21	42·06	41·75

The platinum-salt of ammonium contains 44·22 per cent. of platinum, and that of methylammonium 41·68.

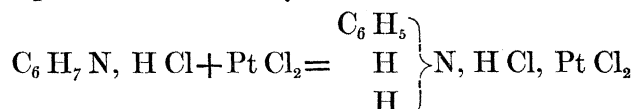
has a perfectly definite and constant composition, it is soluble in water and may be re-crystallized from it. The analyses of samples of different preparations gave us the following results:—

I. 0.467 grm. of the platinum-salt gave	{ 0.216 grm. of carbonic acid. 0.129 grm. of water.
II. 0.219 grm. of the platinum-salt gave	0.082 grm. of platinum.
III. 0.272 grm. of the platinum-salt gave	0.102 grm. of platinum.
IV. 0.308 grm. of the platinum-salt gave	0.1155 grm. of platinum.
V. 0.2725 grm. of the platinum-salt gave	0.1025 grm. of platinum.
VI. 0.099 grm. of the platinum-salt gave	0.03725 grm. of platinum.

These results, translated into percentages, lead to the following numbers:—

	I.	II.	III.	IV.	V.	VI.
Carbon . .	12.61	—	—	—	—	—
Hydrogen .	3.07	—	—	—	—	—
Platinum. .	—	37.44	37.5	37.5	37.61	37.62

The formula of the platinum-salt of allylamine



requires the following theoretical values:—

	Theory.	
6 equivs. of Carbon . . . .	36	13.68
8 equivs. of Hydrogen . . . .	8	3.05
1 equiv. of Nitrogen . . . .	14	5.31
3 equivs. of Chlorine . . . .	106.5	40.46
1 equiv. of Platinum . . . .	98.7	37.50
1 equiv. of Platinum-salt . . .	263.2	100.00

The same body is likewise formed by the action of ammonia upon the iodide of allyl. On distilling the product of this reaction with potassa, ammonia is disengaged; but towards the end of the operation an alkaline liquid distils over, which no longer contains ammonia, and upon which there floats a small quantity of a basic oil. On saturating the aqueous solution, together with the oil, with hydrochloric acid, and adding bichloride of platinum, the platinum salt of allylamine separates either directly, if the solution be concentrated, or gradually, in magnificent gold-coloured needles, if the liquid be gently evaporated.

0.183 grm. of the salt gave on ignition 0.0685 grm. = 37.43 per cent. of platinum.

#### *Diallylamine.*

Impure allylamine, obtained either by the action of potassa on the cyanate, or of

ammonia on the iodide of allyl, when digested with a second quantity of iodide of allyl, is rapidly changed into a mass of hydriodates of new compounds.

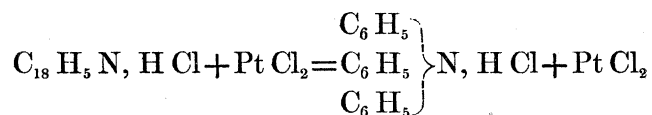
This crystalline mass evidently contains a considerable quantity of the hydriodate of diallylamine; but to succeed in separating it from this very complicated mixture would have required a considerable quantity of substance. We have therefore been satisfied to determine by a few experiments the existence of triallylamine and the oxide of tetrallylammonium.

*Triallylamine.*

The oxide of tetrallylammonium, to which we shall presently allude, submitted to the action of heat, is decomposed with liberation of a basic oil. The experiment was not made on a sufficient scale to admit of the study of the complementary products. The perfect analogy of the oxide of tetrallylammonium with the corresponding ethyl-compound, leaves no doubt respecting the nature of the basic substance which results from its decomposition by the action of heat. This body must obviously be triallylamine, and experiment has confirmed this anticipation. The base saturated with hydrochloric acid and mixed with bichloride of platinum, deposits a yellow platinum-salt, the analysis of which has furnished the following results:—

0·1815 grm. of the platinum-salt gave 0·0515 grm. of platinum.

The formula



represents the following values:—

	Theory.		Experiment.
18 equivs. of Carbon . .	108	31·47	—
4 equivs. of Hydrogen . .	16	4·66	—
1 equiv. of Nitrogen . .	14	4·08	—
3 equivs. of Chlorine . .	106·5	31·03	—
1 equiv. of Platinum . .	98·7	28·76	28·37
1 equiv. of Platinum-salt	343·2	100·00	

*Hydrated Oxide of Tetrallylammonium.*

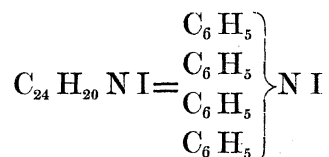
The chief product of the action of ammonia upon iodide of allyl is a magnificent crystalline compound, which is deposited from the solution resulting from the reaction. We have treated iodide of allyl with ammonia in sealed tubes, but this is not necessary, for iodide of allyl is rapidly attacked even by an aqueous solution of ammonia at the common temperature. By contact for a few days a large quantity of the iodide dissolves, and the solution sometimes becomes a solid mass. If no deposition of crystals take place from the solution, it is only necessary to add a concentrated solution of potassa; this causes the separation of an oily layer which speedily solidifies. The crystals thus



formed are the iodide of tetrallylammonium, which, like the corresponding compound of the ethyl- and methyl-series, is but slightly soluble in solution of potassa. It is obtained pure by exposing it to the air until the potassa is converted into carbonate, and then recrystallizing it from absolute alcohol.

On analysis, 0·3805 gramm. of the iodide gave 0·2905 gramm. of iodide of silver.

The formula



leads to the following values :—

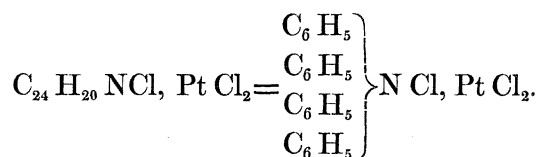
	Theory.		Experiment.
24 equivs. of Carbon . . . . .	144	47·20	—
20 equivs. of Hydrogen . . . . .	20	6·55	—
1 equiv. of Nitrogen . . . . .	14	4·59	—
1 equiv. of Iodine . . . . .	127·1	41·66	41·26
1 equiv. of Iodide of tetrallylammonium	305·1	100·00	

The iodide, treated with oxide of silver, is immediately transformed into the oxide. This forms an alkaline solution, which possesses all the properties of the hydrated oxide of tetrethylammonium. When it is mixed with hydrochloric acid and bichloride of platinum, a pale yellow precipitate is obtained, of which the following is an analysis :—

I. 0·21 gramm. of the platinum-salt gave 0·288 gramm. of carbonic acid and 0·0987 gramm. of water.

II. 0·311 gramm. gave 0·0805 gramm. of platinum.

These numbers lead to the formula



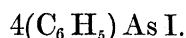
	Theory.		Experiment.	
			I.	II.
24 equivs. of Carbon . . . . .	144	37·57	37·40	—
20 equivs. of Hydrogen . . . . .	20	5·24	5·19	—
1 equiv. of Nitrogen . . . . .	14	3·65	—	—
3 equivs. of Chlorine . . . . .	106·5	27·79	—	—
1 equiv. of Platinum . . . . .	98·7	25·75	—	25·88
1 equiv. of Platinum-salt . . . . .	383·2	100·00		

The examination of the allylamines is far from complete ; we have not succeeded in separating these bodies from one another with sufficient accuracy to give a precise

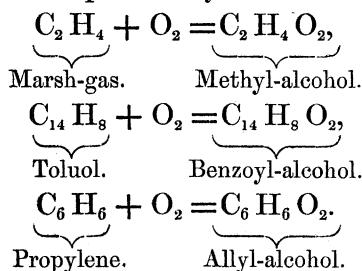
account of the physical properties of the different terms of this series; nevertheless our experiments prove the existence in the allyl-series of four compounds analogous to the four bases of the ethyl-series.

*Iodide of Tetrallylarsonium.*

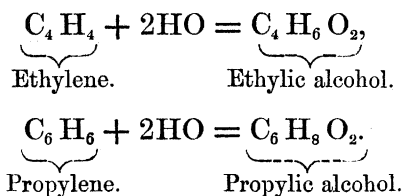
Iodide of allyl attacks arsenide of potassium, but far less energetically than iodide of ethyl; several liquid compounds, of very fetid odour, are produced, the boiling-points of which, however, extend over so considerable a range of the scale, that we had to abandon our desire of studying them. At the same time a solid crystalline body is formed which is obviously iodide of tetrallylammonium, in which the nitrogen is replaced by arsenic,



On reviewing the preceding results, it is obvious that propylene, a homologue of ethylene, is susceptible of furnishing a mono-acid alcohol and its derivatives, which bears to ethylene the same relation that is observed between methyl-alcohol and marsh-gas, or between benzoic alcohol and toluol, the analogue of marsh-gas among the derivatives of the aromatic acids. The hydrocarbons homologous with, and analogous to marsh-gas, the homologues of ethylene, and indeed probably a very considerable number of other similarly constituted hydrocarbons, may be regarded as starting-points for the preparation of mono-acid alcohols and their derivatives. All these alcohols are formed by the fixation of two equivalents of oxygen, which oxidation, however, cannot yet be effected directly, but is accomplished by a series of substitution-processes.



Olefiant gas and its homologues are capable of furnishing mono-acid alcohols by another reaction, which has not yet been applied to the series of bodies homologous with marsh-gas. In fact, we have learnt by the researches of M. BERTHELOT, that olefiant gas and its homologues are capable of being transformed into alcohols by the absorption of two equivalents of water; olefiant gas furnishes by this reaction ordinary alcohol; and propylene, propylic alcohol; thus—



Olefiant gas, then, and all its homologues are capable of furnishing *two* mono-acid alcohols, exhibiting slightly different features, but presenting in all their principal characters the most obvious analogies. The alcohols formed by fixation of water, such as ethylic alcohol, have been long well known; in fact the detailed study which has been made during the last quarter of a century of most of their derivatives, has exercised the most important influence upon the development of organic chemistry.

The same remark does not apply to the alcohols produced from these same hydrocarbons by fixation of oxygen. The history of allylic alcohol, which we have endeavoured to trace in the preceding pages, and to which of late important contributions have been furnished by MM. BERTHELOT and DE LUCA and by M. ZININ, begins also to throw light upon this second group of alcohols. For this reason, the discovery of allylic alcohol appears to claim the attention of chemists, even had it not assisted in fixing, in the system of organic compounds, the exact position of several very interesting natural products, viz. the sulphuretted oils furnished by the bulbs of the garlic (*Allium sativum*) and the seeds of the black mustard (*Sinapis nigra*), which it had not been possible up to the present time to group around a similar centre.

It is highly probable that by submitting the various hydrocarbons polymeric with propylene to appropriate reactions, other alcohols may be obtained homologous with allyl-alcohol. This much is certain, that by distilling a mixture of cyanate of silver and bromide of amylene,  $C_{10}H_9Br$ , a volatile liquid is obtained, which possesses an extremely irritating odour, causing lacrymation like the cyanic ethers. This forms by contact with ammonia a crystallizable urea, which, when decomposed by potassa, yields, like cyanate of allyl, bases, among which the compound  $C_{10}H_{11}N$  may be traced.

Allylic alcohol, the history of which we have endeavoured to sketch, forms the third term of a series of alcohols, which may be represented by the general formula



In fact, a group of homologous acids is known, which, according to their composition, bear the same relation to acetic acid and its homologues, that is observed between our new group of alcohols, and the alcohol-series commencing with methylic and ethylic alcohols. In addition to acrylic acid, angelic and oleic acids are the best known terms of this group of acids. It is possible that cyanide of allyl, which is formed by the double decomposition of iodide of allyl and cyanide of silver, but which we have not yet been able to obtain in a state of sufficient purity to admit of analysis, may be transformed by boiling with a solution of caustic potassa into an acid homologous with acrylic acid, in the same way as cyanide of propyl is resolved under similar circumstances into butyric acid.

We conclude this paper with a Table which exhibits in a perspicuous manner the two groups of alcohols and acids.

Alcohols.		Acids.	
$C_2 H_4 O_2$ Methylic.	$C_2 H_2 O_2$	$C_2 H_2 O_4$ Formic.	—
$C_4 H_6 O_2$ Ethylic.	$C_4 H_4 O_2$	$C_4 H_4 O_4$ Acetic.	$C_4 H_2 O_4$
$C_6 H_8 O_2$ Propylic.	$C_6 H_6 O_2$ Allylic.	$C_6 H_6 O_4$ Propionic.	$C_6 H_4 O_4$ Acrylic.
$C_8 H_{10} O_2$ Butylic.	$C_8 H_8 O_2$	$C_8 H_8 O_4$ Butyric.	$C_8 H_6 O_4$
$C_{10} H_{12} O_2$ Amylic.	$C_{10} H_{10} O_2$	$C_{10} H_{10} O_4$ Valeric.	$C_{10} H_8 O_4$ Angelic.
$C_{12} H_{14} O_2$ Caproylic.	$C_{12} H_{12} O_2$	$C_{12} H_{12} O_4$ Caproic.	$C_{12} H_{10} O_4$
$C_{14} H_{16} O_2$	$C_{14} H_{14} O_2$	$C_{14} H_{14} O_4$ Enanthylic.	$C_{14} H_{12} O_4$
$C_{16} H_{18} O_2$ Caprylic.	$C_{16} H_{16} O_2$	$C_{16} H_{16} O_4$ Caprylic.	$C_{16} H_{14} O_4$
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
$C_{36} H_{38} O_2$	$C_{36} H_{36} O_2$	$C_{36} H_{36} O_4$ Stearic.	$C_{36} H_{34} O_4$ Oleic.

A glance at this Table shows how very few representatives of the series of alcohols  $C_{2n} H_{2n} O_2$ , and acids  $C_{2n} H_{2n-2} O_4$ , have as yet been observed. The progress of science will not fail to fill up the numerous gaps.

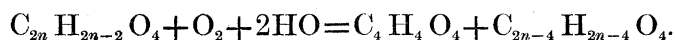
Even now some bodies are known which are most intimately connected with the preceding series. Indeed, cinnamic alcohol and cinnamic acid belong to a group of substances bearing to the aromatic alcohols and acids the same relation which obtains between the allyl-compounds and their homologues, and the alcohols and acids of the fatty bodies.

Alcohols.		Acids.	
$C_{14} H_8 O_2$ Benzoic.	$C_{14} H_6 O_2$	$C_{14} H_6 O_4$ Benzoic.	$C_{14} H_4 O_4$
$C_{16} H_{10} O_2$	$C_{16} H_8 O_2$	$C_{16} H_8 O_4$ Toluic.	$C_{16} H_6 O_4$
$C_{18} H_{12} O_2$	$C_{18} H_{10} O_2$ Cinnamic.	$C_{18} H_{10} O_4$	$C_{18} H_8 O_4$ Cinnamic.
$C_{20} H_{14} O_2$ Cuminiic.	$C_{20} H_{12} O_2$	$C_{20} H_{12} O_4$ Cuminiic.	$C_{20} H_{10} O_4$

From this Table, again, it is manifest how many substances remain still to be discovered in this direction. Cinnamic acid contains two equivalents of hydrogen less than the acid

$C_{18}H_{10}O_4$ , which will be discovered between toluic and cuminic acids. It stands to this acid in the same relation as acrylic stands to propionic acid.

The acids belonging to the acrylic group all possess the property of being transformed, by fixation of two atoms of oxygen and two of water, into acetic acid and a second homologous acid, as is shown by the following equation:—



It is thus that acrylic, angelic, and oleic acids are resolved under the influence of hydrate of potassa at a temperature of  $200^\circ$  C. into acetic acid, and into formic, propionic, and ethalic acids.

Cinnamic acid suffers under the influence of fusing potassa a perfectly analogous transformation. This acid fixes two equivalents of oxygen and two equivalents of water, and yields acetic and benzoic acids.

In carrying out the preceding inquiry, we have been very ably assisted by Mr. ARTHUR H. CHURCH, to whom our best thanks are due.